Porous Capsules

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Softening of Pore and Interior Properties of a Metal-Oxide-Based Capsule: Substituting 60 Oxide by 60 Sulfide Ligands**

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In memory of Jerzy Haber

The discovery of fullerenes[1] has induced considerable interest in spherical molecular clusters, see for example Refs. [2–5]. Among fullerene-like molecules, spherical water-soluble metal-oxide-based nanocapsules of the type $\{(M^{VI})M^{VI}_5\}_{12}(linker)_{30}$ (M = Mo or W), belonging to the family of Keplerates,[5,6] show quite attractive features in the context of nano- and materials science, especially in confined scenarios.[7–9] Correspondingly, they have been the focus of reviews[10,11] and highlights, including some in recent textbooks.[12] The nanocapsules contain 12 metal-oxide-based pentagonal units linked by either mononuclear (e.g. Fe^{3+}, Cr^{3+} or VO^{2+})[7b] or dinuclear ($\{Mo^{V}_2O_4\}^{2+}$) spacers and 20 pores/channels.[10,11] In case of the Mo_{132}-type cluster, the interiors of the capsules can be fine-tuned by changing the internal ligands coordinated to the $\{Mo^{V}_2O_4\}$ linkers. Most importantly, the above-mentioned Keplerates can interact specifically with their environment.[10–12] Especially the crown ether-type $\{Mo_9O_9\}$ pores can react through hydrogen bonding with organic cations (like the guanidinium, amidinium, or protonated urea type),[13] as well as with hydrated metal ions, whereby all act as plugs leading to the closing of the capsules.[14] The 20 smaller $\{M_3M'_3O_6\}$ pores of the negatively charged $M_{72}M'_{30}$-type Keplerates (M = Mo^{VI}, W^{VI}; M′ = V^{IV}, Fe^{III}) have a high affinity for K^+ and NH_4^+ ions similar to 18-crown-6 receptors;[15] this corresponds to sphere surface supramolecular chemistry. The present type of Keplerates also has the potential for being used as nanoreactors.[16] Replacement of the bridging oxo ligands of the above-mentioned $\{Mo^{V}_2O_4\}$ linkers by softer sulfido ligands provides a new option to change the properties/reactivities of Mo_{132}- and $W_{72}Mo_{60}$-type capsules. This change of linkers has now been achieved: We report here the synthesis, crystal structure, and spectroscopic characterization of $W_{72}Mo_{60}$-type capsules with $\{Mo^{V}_2O_2(\mu\text{-}S)_2(L)\}$ linkers (L = CH_3COO^-). The important result is that the pore sizes and reactivities/flexibilities as well as the interior capsule properties—also in context of an increase in the internal shell polarizability—are changed by substituting 60 oxide atoms of the known Keplerate containing $\{Mo^{V}_2O_4\}$ linkers by 60 sulfide atoms; this has, for example, consequences for ligand and cation uptake/release processes[17] as well of course as for the structure of encapsulated species.

The synthesis process follows that of previously reported mixed metal Keplerates where the basic $\{(M^{VI})M^{VI}_5\}$-type units (M = Mo, W) form in solution according to the principles of "Constitutional Dynamic Chemistry" of Lehn[18] while finally 12 of the units get appropriately linked when cations, like $\{Mo_2O_4(aq)\}^{2+}$,[19] $VO(aq)^{2+}$,[15a] or $Fe(aq)^{3+}$[15b] are added to a dynamic library of molybdates and tungstates. In the present case, an aqueous solution of the new dinuclear linker $\{Mo^{V}_2O_2(\mu\text{-}S)_2(aq)\}^{2+}$—prepared by hydrolysis of the oxo/thio compound usually used as a source of $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}^{2+}$[20]—allowed to obtain the water-soluble Keplerate-type compound **1** (which allows future reactivity studies in solution) as starting material for the less soluble compound **2**[***] which was isolated by "recrystallization" of the nonrecrystallized **1** in the presence of cobalt (II) ions to get suitable crystals (for details see the Experimental Section). Whereas compound **1** could be only partially characterized because of the poor crystal quality (for the "approximate" formula see Experimental Section), this was not the case for compound **2** which is the focus of our present work. Compound **2**, which crystallizes in the space group *Immm*, was fully characterized by elemental analysis,

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[***] $Co_{12}[\{W^{VI}_6O_{21}(H_2O)_6\}_{11}\{W^{VI}_6O_{21}(H_2O)(H_2Mo^{VI}_2O_8(H_2O))\}\{Mo^{V}_2O_2S_2(CH_3COO)\}_{10}\{Mo^{V}_2O_2S_2(H_2O)_2\}_{20}]$·ca. $\{11[(CH_3)_4N]^+ + 8\,Na^+ + 11\,CH_3COO^- + 4\,SO_4^{2-} + 350\,H_2O\} \equiv Co_{12}$·**2a**·lattice ingredients ≡ **2** (formally written regarding the cation positioning).

spectroscopic methods (IR, UV/Vis, and X-ray photoelectron spectroscopy), magnetic suceptibility measurements and single-crystal X-ray structure analysis (see Ref. [21] and the Experimental Section).

The obtained $W_{72}Mo_{60}$-type cluster **2a** belongs to the family of porous capsules having the general composition $\{(M^{VI})M^{VI}_5\}_{12}\{Mo^{V}_2O_2(\mu\text{-}X)_2\}_{30}$ (M = Mo or W; X = O or S). The 12 centers of the pentagonal $\{(W^{VI})W^{VI}_5\}$-type units are positioned at the vertices of an icosahedron and are connected by 30 $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}^{2+}$ linkers, the Mo atoms of which span a distorted truncated icosahedon (Figure 1); for general aspects of the related problem of interpenetrations of the

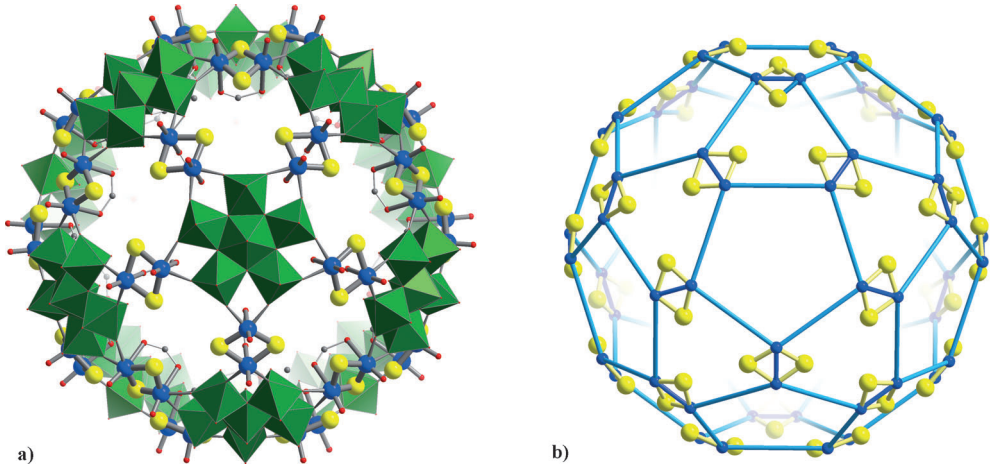

Figure 1. a) Combined polyhedral/ball-and-stick picture of **2a** with view along a five-fold symmetry axis highlighting a central pentagonal $\{(W^{VI})W^{VI}_5\}$-type unit (which can be considered as a ligand[7c]) and five related $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ linkers (stabilized by acetate ligands) as well as the pores which are obviously decreased in size by substituting oxide by sulfide ligands ($\{(W^{VI})W^{VI}_5\}$ groups in polyhedral representation green, Mo blue, S yellow, O red, C grey spheres). b) Structure of the $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}_{30}$ fragment, of which the Mo atoms form a distorted truncated icosahedron with 12 regular pentagons and 20 (trigonal) hexagons (60 Mo–S–Mo bridges in yellow and 30 Mo^{V}–Mo^{V} bonds in dark blue).

Platonic and Archimedean solids see Refs. [3a, 5, 6a]. Ten CH_3COO^- are bound as bidentate bridging ligands to the Mo atoms of the 10 dinuclear linkers and 2×20 monodentate H_2O ligands to the Mo atoms of the other 20 (see the formula).

The average Mo–Mo distance of 2.84 Å is in close agreement with the corresponding values in dinuclear complexes containing the $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ core,[22] but is—as expected—larger than in the $\{M^{VI}_{72}Mo^{V}_{60}\}$-type Keplerates with the $\{Mo^{V}_2O_4\}$ linkers (2.58 Å for M = Mo[23a] and 2.57 Å for M = W[19]). The Mo–S–Mo bridges are nearly symmetrical (average Mo–S distance: 2.31 Å) and the average distance from the center of the pores, spanned by the three bridging S atoms to each of the latter atoms, is 3.00 Å (see Figure S1 in the Supporting Information); this gives, based on a van der Waals radius of S of 1.80 Å,[24] an indication of the geometric pore size, whereas the effective one depends on the experimental conditions. Anyhow the opening and receptor properties of the $\{W_3Mo_6O_6S_3\}$ pore are significantly different from those of the $\{Mo_9O_9\}$ and $\{W_3Mo_6O_9\}$ pores in the $\{Mo_{132}\}$- and $\{W^{VI}_{72}Mo^{V}_{60}\}$-type Keplerates with $\{Mo^{V}_2O_4\}$ linkers[19,23] (see also Figure S1 in the Supporting Information).

A result of general importance refers to the impressive segregation between the mostly hydrophobic internal wall—spanned/influenced by the ten internal acetate ligands—and the encapsulated "water molecule collection" which forms a rather well-defined unprecedented shell with no water molecules inside (for details including distances see Figure S2 in the Supporting Information). This type of "water" under confined conditions has unique properties[25] ("water" in hydrophobic cavities is considered to be of tremendous interdisciplinary interest[25]). One fascinating aspect is that one can tune the "water assembly" by changing the ratio of acetate and water ligands. But as this is not our major topic here it will be discussed in detail in the future (see also related comments in our recent publication[25]).

The IR spectrum of **2** shows—in addition to the very characteristic molybdenum-oxide-based band pattern of the $\{M^{VI}_{72}Mo^{V}_{60}\}$ clusters[19,23]—the bands of stretching vibrations of the acetate ligands. The band at 457 cm^{-1} is assigned to ν_{as}-(Mo–S–Mo) stretching modes of the linkers (see Figure S3 in the Supporting Information for further details).

The stability of the $\{(W)W_5\}_{12}\{Mo_2O_2S_2\}_{30}$ skeleton in solution had to be proven by measuring the Raman spectrum of the soluble compound **1**—an important aspect for future studies. The very characteristic spectrum for the spherical/icosahedral system—showing correspondingly only a very few intense lines (see also Refs. [11e, 19])—is shown in Figure S4 in the Supporting Information, together with correspondingly similar ones of the related $\{(W)W_5\}_{12}\{Mo_2O_4\}_{30}$-[19] and $\{(Mo)Mo_5\}_{12}\{Mo_2O_4\}_{30}$-type[23] clusters; the comparison allows to get information about the capsule property changes due to the replacement of molybdenum by tungsten atoms. This leads to different M=O bond strengths and bond polarizabilities as well as to different interactions of the metal atoms with the internal ligands (see the Supporting Information with additional literature for a detailed discussion). Preliminary NMR studies of the solution have also been performed (see the Supporting Information).

In conclusion, the family of metal-oxide-based $\{(W^{VI})W^{VI}_5\}_{12}\{Mo^{V}_2O_4\}_{30}$-type capsules has been extended to those with $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ linkers, that is, substituting correspondingly 60 oxide by 60 sulfide atoms. The $\{W_3Mo_6O_6S_3\}$-type pores differ from their $\{M_3Mo_6O_9\}$ (M = Mo, W) counterparts with respect to their openings, their flexibilities, and their reactivities, especially in the context of cation and ligand uptake/release processes as well as strength of

interactions of the internal ligands with the metal cations and consequentially the influence on the encapsulated species. Furthermore, the pore affinity for hydrogen-bonded guests/plugs is decreased thereby decreasing the tendency/option of pore closing. Also important, the replacement of 60 oxide by 60 sulfide ligands in the porous capsule skeleton increases the internal shell polarizability which influences reactions inside the capsules and the structure of encapsulated species. These remarks should give rise to corresponding future investigations of solutions of the soluble compound **1**, especially in the context that several materials science problems have been studied based on the metal-oxide-type Keplerates. In this context it is also intended to get structural data for **1**.

Experimental Section

Synthesis of **1** (a precursor for **2**, the focus of our article): A sample of the oxo/thio cluster of empirical composition "$K_{0.4}\{N(CH_3)_4\}_{0.1}I_{0.5}[Mo_2S_2O_2(OH)_2(H_2O)]\cdot 6.3\,H_2O$"[20a] (1.0 g, 2 mmol) was dissolved in hydrochloric acid (4 M, 10 mL) by mild heating (50 °C). The red solution was filtered and added to a solution of $Na_2WO_4\cdot 2\,H_2O$ (4.5 g, 13.64 mmol) and $NaCH_3COO\cdot 3\,H_2O$ (10.0 g, 73.49 mmol) in water (40 mL) acidified to a pH around 4 with 100% acetic acid (18 mL). The milky orange suspension was heated quickly to 80 °C (oil bath temperature) by vigorous stirring in an argon atmosphere before some water (30 mL) was added. The reaction mixture was heated further (120 °C, oil bath temperature) under continuing vigorous stirring until a clear red solution was obtained (after 90 min). The solution was cooled to room temperature, and the red microcrystalline powder that started to precipitate during this time was filtered off, washed thoroughly with ethanol, and dried with diethyl ether (crude product, yield: 0.7 g, around 30% based on Mo). Cubic crystals ($a = 38.0$ Å, $V = 54891$ Å^3) of compound **1** were obtained within 1–2 days by recrystallization of the crude product in water (1 g, 5 mL; yield: 0.6 g). The crystal structure could not be fully refined (poor quality of the crystals), but there is unambiguous evidence that the spherical $W_{72}Mo_{60}$-type Keplerate **1a** is quite similar to **2a** according to results from IR, Raman, UV/Vis and NMR data (note: the numbers of coordinated acetate ligands and $[(CH_3)_4N]^+$ (TMA) ions do not need to be identical). Anyhow in the absence of a detailed crystal structure analysis and on account of the low abundance of several elements, only an approximate formula for compound **1** can be given: $[(CH_3)_4N]_7Na_{25}[\{W^{VI}{}_6O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_2S_2(CH_3COO)\}_{20}\{Mo^{V}{}_2O_2S_2(H_2O)_2\}_{10}]\cdot$ca.$\{8\,Na^+ + 8\,CH_3COO^- + 300\,H_2O\}$ (formally written regarding cation positioning) $\equiv [(CH_3)_4N]_7Na_{25}\cdot$**1**$\cdot$lattice ingredients $\equiv$ **1**. Anal. calc. (%) for: $C_{84}H_{952}Mo_{60}Na_{33}N_7O_{760}S_{60}W_{72}$: C 2.81, N 0.27, S 5.36, Na 2.11, W 36.87; found: C 3.4, N 0.2, S 5.6, Na 2.6, W 39.0. (Na and W analyses were performed by the Forschungszentrum Jülich GmbH, ZCH, 52425 Jülich, Germany.) The formula corresponds to the NMR results, especially regarding the ratio of the total number of TMA ions to the total number of acetate ions, that is, around 4. The vibrational spectra (Raman, IR), UV/Vis and preliminary ^{1}H NMR spectra of **1**, the starting material of **2**, are given in the Supporting Information.

Synthesis of **2**: Crystals of better quality of the less soluble (!) compound were obtained by adding $CoCl_2\cdot 6\,H_2O$ (0.03 g) to a solution of the crude compound **1** (0.2 g) in water (10 mL). Red crystals appeared within 2–3 days. Anal. Calc. (%) for: $C_{86}H_{1013}Co_{12}Mo_{62}Na_8N_{11}O_{786}S_{64}W_{72}$: C 2.8, N 0.42, S 5.56, Na 0.5, Co 1.92 (values refer to the small number of $300\,H_2O$ caused by weathering, see also Ref. [26]); found: C 2.8, N 0.3, S 5.8, Na 0.4, Co 2.1. (S, Na and Co analyses were performed by the Mikroanalytisches Labor Egmont Pascher, An der Pulvermühle 3, 53424 Remagen, Germany). Characteristic UV/Vis bands: 293, 342, 384 (sh) nm. The vibrational data (Raman, IR) of **2** are given in the Supporting Information.

Crystal data for **2**: $C_{86}H_{1113}Co_{12}Mo_{62}Na_8N_{11}O_{836}S_{64}W_{72}$ (refers to $350\,H_2O$), $M = 37813.27$ g mol^{-1}, orthorhombic, space group *Immm*, $a = 34.5430(14)$, $b = 37.5676(14)$, $c = 42.2049(17)$ Å, $V = 54769(4)$ Å^3, $Z = 2$, $\rho = 2.293$ g cm^{-3}, $\mu = 8.608$ mm^{-1}, $F(000) = 35524$, crystal size = $0.20 \times 0.16 \times 0.12$ mm^3. A total of 164400 reflections ($1.45 < \Theta < 27.01°$) were collected, of which 31201 reflections were unique ($R_{int} = 0.1316$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0732$ for 12508 reflections with $I > 2\sigma(I)$, $R = 0.2063$ for all reflections; max/min residual electron density 1.484 and -1.357 e Å^3. Crystals of **2** were removed from the mother liquor and immediately cooled to 173(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, MoKα radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5 cm). (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1997/2001; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001.) CCDC 831156 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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